1 Combination of a crop model and a geochemical model
2 as a new approach to evaluate the sustainability of an
3 intensive agriculture system

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6 **Abstract**

7 By combining a crop model (STICS) and a geochemical model (PHREEQC),
8 a new approach to assess the sustainability of agrosystems is proposed. It is
9 based upon aqueous geochemistry and the stepwise modifications of soil so-
10 lution during its transfer from the surface till aquifer. Meadows of Crau (SE
11 France), irrigated since the 16th century, were field monitored (2012-2015)
12 and modelled. Except for N, the mineral requirements of hay are largely
13 covered by dissolved elements brought by irrigation water with only slight
14 deficits in K and P, which are compensated by P-K fertilizers and the winter
15 pasture by sheep. N cycle results in a very small nitrate leakage. The main
16 determinants of the chemical composition changes of water are: concentra-
17 tion by evaporation, equilibration with soil pCO₂, mineral nutrition of plants,
18 input of fertilizers, sheep grazing, mineral-solution interactions in superficial
19 formations till the aquifer, including ion exchange. Inverse modelling with
20 PHREEQC allows for quantifying these processes. For groundwater, mea-
21 sured composition fit statistically very well with those computed, validating
22 thus this approach. This long-term established agrosystem protects both soil
23 and water resources: soil nutritional status remains constant with even some
24 P and (minor) K fixation in soils; long-term decarbonation occurs but it is
25 greatly slowed by saturation of irrigation water by carbonate; P fixation in
26 soil protects groundwater from eutrophication.

27 **Keywords:** Biogeochemical modelling, Mineral flux, Irrigation, Meadow,
28 Water quality

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29 1. Introduction

30 In the circumstances of global changes, *i.e.* urban sprawl and climate
31 change, risks of degradation of natural and agricultural environments increase
32 and territories become more vulnerable (Pachauri et al., 2007; Zhang et al.,
33 2007; Pageaud and Carré, 2009; Oliso et al., 2013; Baillieux et al., 2015;
34 Trolard et al., 2016). Climate change may positively or negatively impact
35 the services provided by ecosystems on which our social systems depend
36 (Trolard and Dangeard, 2014).

37 To ensure the resilience of a territory face to these changes, we must start
38 from the concepts of limited space, scarce resources especially soil and water
39 and integrate information (Trolard et al., 2013b).

40 It is recognized that irrigated systems can regulate the local climate, water
41 resources and food security but little attention has been spent to the influence
42 of nutrients in irrigation water, except in the special case of the application of
43 treated wastewater for agricultural irrigation, which could provide nutrients
44 and provide economic benefits (Cromer et al., 1984; Bureau et al., 1987; Asano,
45 1998; Shuval, 1991; Oron et al., 1995; Lubello et al., 2004; Bixio et al., 2006;
46 Tsiridis et al., 2009; Angelakis and Bontoux, 2001). Water scarcity and
47 increase of costs of fertilizers make a more rigorous evaluation of water use
48 in agriculture necessary.

49 Groundwater and surface water are not isolated. Thereby, any develop-
50 ment or contamination of one normally affects the other and the general com-
51 position of rivers (Livingstone, 1963; Sophocleous, 2002; Goren et al., 2014).

52 Irrigation water directly influences groundwater quality: nutrient fluxes were
53 paid a lot of attention to (Valett et al., 1996; Dahm et al., 1998; Bourg and
54 Bertin, 1993; Gibert et al., 1997; Sophocleous, 2002).

55 The processes at the interface between surface water and groundwater
56 affect solute retention in streams (Valett et al., 1996) and lateral nutrient
57 fluxes between uplands and aquatic ecosystems (Dahm et al., 1998; Wallis
58 et al., 1981; Grimm and Fisher, 1984).

59 In coastal areas, phreatic water exerts a pressure on sea water to pre-
60 vent salt intrusion and protects resource for drinking water, agricultural and
61 industrial needs, including tourism (Mayer et al., 2016).

62 Other studies revealed that plant activity enriches the upper part of soils
63 with inorganic elements used during growth (*e.g.* Si, K, Ca, Mg) (Jobbágy
64 and Jackson, 2001; Lucas, 2001; Barré et al., 2009). Some studies have
65 provided evidence of plants accelerating silicate weathering and CO₂ con-
66 sumption (Alexandre et al., 1997; Kelly et al., 1998; Moulton et al., 2000;
67 Hinsinger et al., 2001; Song et al., 2011, 2012).

68 These studies point to the important role of plant to modify mineral
69 balance of soil solution. Nevertheless, accounting for plant uptake is rather
70 crude in biogeochemical modelling especially for daily uptake of inorganic
71 elements by plants (Hartman et al., 2007).

72 In this context, the aim of this paper is to assess the sustainability of an
73 intensive agricultural system under mediterranean to semi-arid climate.

74 The components of sustainability addressed here are: i) the short-term

75 nutritional status of soils ; ii) the long-term tendency of soils towards decar-
 76 bonatation and acidification, and iii) the quality of phreatic groundwater as
 77 a regional resource. Our approach combines a crop model (STICS) and a
 78 geochemical model (PHREEQC) and is based upon aqueous geochemistry to
 79 simulate the stepwise modifications of soil solution during its transfer from
 80 the surface till aquifer. Though PHREEQC is basically a geochemical model,
 81 it is here extended for the first time to simulation of uptake of elements by
 82 plants, and use of proton balance allows for taking into account the rhizo-
 83 sphere effect of acidification of soil solution.

84 2. Modelling

85 2.1. State of the art on biogeochemical models

86 Different models combine geochemical processes in agroecosystems, as
 87 illustrated in table 1. Most models have been developed for specific purposes:
 88 *e.g.* N and C cycles, acid rain or stress effects on forests.

89 Heat, water, nitrogen (N) and carbon (C) fluxes are simulated in many
 90 models of soil-plant-atmosphere system (Cramer et al., 2001; Morales et al.,
 91 2005; Yu et al., 2006; De Kauwe et al., 2013; Forster et al., 2013; Friedling-
 92 stein et al., 2014; Walker et al., 2014; Wenzel et al., 2014; Sándor et al.,
 93 2016; Senapati et al., 2016; Zhang et al., 2016), but do not pay attention to
 94 inorganic elements.

95 Nitrogen transport is studied through linking the hydrological flowpath
 96 and biogeochemical pathway in saturated / near-stream zones: this shows

that surface / groundwater exchanges change rapidly on the timescale of hydrologic events, which controls the fate of N (Cirmo and McDonnell, 1997).

Solute retention in streams and lateral nutrient fluxes are modelled by linking hydrologic retention, biological nutrient cycling and chemical processes at the surface water / groundwater interface (Valett et al., 1996; Dahm et al., 1998).

Two models, PaSim and Biome-BGC MuSo, linking climate, soil, vegetation and management to ecosystem biogeochemical cycles were compared to simulate C cycle (Sándor et al., 2016), and fluxes between the terrestrial biosphere and the atmosphere in the context of the global change (Xiao et al., 2012; Cramer et al., 1999; Jung et al., 2007; Huntzinger et al., 2012).

Soil chemical and biological properties are combined to assess how nutrients cycling could be affected by wildfire (Fultz et al., 2016). The alpine hydrochemical model (AHM) gathered hydrological, geochemical, climatic and biogeochemical data sets to simulate daily stream chemical composition and its reaction to N deposition, but it cannot reflect terrestrial nutrient cycling (Meixner et al., 2000). SOILVEG and the combined FORGRO/NUCSAM gather biogeochemical and canopy processes to study effects of multiple stressors on forest stands, but they do not simulate stream chemistry (van Heerden et al., 1995; Mohren and van de Veen, 1995).

To capture ecosystem and surface water chemical response to atmospheric deposition and climate, biogeochemical model is established to simulate soil and surface water chemistry by linking ecosystem model (DayCent) with

120 geochemical model (PHREEQC), nevertheless this model simulates only C,
121 N, P, and S dynamics, there is no assimilation of cations (Ca^{2+} , Mg^{2+} , K^{+})
122 by plants (Hartman et al., 2007).

123 None of the preceding combination of models include both crop models
124 for grassland ecosystems and biogeochemical models with their influence on
125 soil solution and water quality.

126 Crop models can provide daily simulations of growth, but daily plant
127 chemical analyses are very complicated and expensive to obtain.

128 2.2. Biogeochemical processes

129 Many processes influence the chemical composition of soil solution (Fig.
130 1): evapotranspiration, exchange of matter with soil and plants, inputs of
131 fertilizers and manure (Mohammed et al., 2016b) and ion exchange. Thus
132 it is necessary to acquire data on: i) the chemical composition of irrigation
133 water and groundwater; ii) the nature and quantities of fertilizers and manure
134 input on grassland soils; iii) the quantities of chemical elements harvested
135 and exported during the various cuts of hay; iv) the effect of winter grazing
136 meadows by sheeps, and v) pCO_2 and temperature conditions in the soil.

137 The approach is based on combination of existing models, namely the crop
138 model STICS, (Simulateur mulTIdisciplinaire pour les Cultures Standard)
139 (Brisson et al., 2008) and the geochemical model PHREEQC (pH-REdox-
140 EQUilibrium written in C language) (Parkhurst and Appelo, 2013) (Fig. 2).
141 This interface is a part included in the general PRECOS framework approach

142 (Trolard et al., 2016). Basic principles of both models are given below.

143 STICS is a crop model, such as CERES, PANORAMIX, SUNFLO, PASIM,
144 GRAECO (Brisson and Levraut, 2010). More specifically, STICS simulates
145 the behavior of the soil-crop system in daily time step within 1 year. The up-
146 per limit of the system is the atmosphere characterized by standard climatic
147 variables (solar radiation, minimum and maximum temperature, precipita-
148 tion, reference evapotranspiration) and the lower limit corresponds to the
149 soil/subsoil interface. STICS model is composed of seven modules: growth,
150 development, shoot and root growth, yield components, thermal environ-
151 ment, water balance and nitrogen balance (Brisson et al., 2008). Leaf area
152 index is a dynamic parameter used to simulate radiative budget, taking into
153 account the morphology of plant cover. Carbon assimilation is simulated with
154 detailed biochemistry of photosynthesis and gross respiration. The effect of
155 CO₂ on stomatal resistance is taken into account to compute the budget of
156 radiative and convective energies. Water is transferred in soil to the underly-
157 ing horizon as soon as water holding capacity is exceeded. For organic matter
158 evolution, N cycle is first simulated, then C evolution is derived, by assuming
159 a constant value of C/N ratio (Brisson and Levraut, 2010).

160 STICS takes into account climate, soil characteristics, the type of crop
161 and crop management. Its outputs are the production (yield and quality of
162 biomass), and water and nitrogen balances. STICS was adapted for grassland
163 (Ruget et al., 1999) and tested with success for various types of grasslands
164 (Ruget et al., 2006).

165

166 PHREEQC (Parkhurst and Appelo, 1999, 2013) is designed to perform a
167 wide variety of low-temperature aqueous geochemical calculations. PHREEQC
168 is based on an ion-association aqueous model and has capabilities for : (1)
169 speciation and saturation-index calculations; (2) batch-reaction and one-
170 dimensional (1D) transport calculations involving reversible reactions, which
171 include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-
172 exchange equilibria, and irreversible reactions, which include specified mole
173 transfers of reactants, kinetically controlled reactions, mixing of solutions,
174 and pressure and temperature changes; and (3) inverse modelling, which
175 finds sets of mineral and gas mass transfers that account for differences in
176 composition between waters, within specified compositional uncertainty lim-
177 its. It calculates the degree of saturation indexes ($SI = \log IAP - \log K(T)$),
178 where IAP is the Ionic Activity Product and K is the equilibrium constant
179 of the reaction at temperature T for various minerals (calcite, gypsum etc.),
180 changes in the water quality during its pathway through the soil, the amounts
181 of dissolved or precipitated minerals, ion exchange and surface complexation
182 phenomena.

183 In every case, PHREEQC can calculate changes in the chemical compo-
184 sition of the soil solution. PHREEQC takes thus into account the major
185 geochemical processes that determine the water quality in a “water - plant -
186 soil - atmosphere” system (WPSA).

187 PHREEQC has been combined with hydrological models to simulate pro-

cesses in deep aquifers, oil fields or geothermal energy production systems,
assessment of contaminants or elements transport in watershed and to assess
the hydrogeochemistry of seawater intrusion (Van Berk et al., 2009; Bozau
et al., 2015; Papassiopi et al., 2014; Korrani et al., 2015; Garneau et al.,
2017; Boluda-Botella et al., 2014; Rezaei et al., 2005), simulation of dis-
solved organic carbon (DOC) degradation using first-order kinetics, assuming
two DOC fractions differing in reactivity (van Breukelen et al., 2004), and
for predicting and designing biodenitrification applications including in the
model microbiological processes - exogenous and endogenous nitrate respira-
tion coupled to microbial growth and decay (Rodríguez-Escales et al., 2014).
Inverse modelling was used to explain the modifications of the geochemistry
of groundwaters of the three main aquifers of Sahara (Slimani et al., 2016).

2.3. STICS Outputs used to interface with PHREEQC

From climatic data, rainfall P , temperature t , irrigation I , and crop pa-
rameters, STICS calculates many parameters, of which a few are used here
to interface with PHREEQC, namely: (i) evapotranspiration ET , (ii) the
amount of water that drains below the root system into the deeper horizons
of soil (drainage D), (iii) growth and the amount of biomass produced (yield
 R).

All these output data, *measured during the same time interval*, are used
to calculate the factor of water concentration by evaporation (Table 2) as :

$$f_c = \frac{P + I}{P + I - ET} = \frac{P + I}{D}. \quad (1)$$

209 The P , I , R and D quantities provided by STICS allow for computing
 210 fluxes (mass/unit area) from concentrations of elements in plants (mass of
 211 element/kg of dry matter DM), in irrigation water, groundwater and soil
 212 solution (mass/volume of soil solution).

213 The flux of inorganic element exported by crop (Q_b) is given by:

$$Q_b = R[E]_b, \quad (2)$$

214 where $[E]_b$ is the concentration of an element E in plant (biomass) (mol kg^{-1}
 215 DM), and R the yield of exportation (kg of DM m^{-2}), and Q_b is in mol m^{-2} .

216 The flux of inorganic element brought by irrigation water is given by:

$$\begin{aligned} Q_p &= P\rho_w[E]_p + I\rho_w[E]_I, \\ &\simeq I\rho_w[E]_I, \end{aligned} \quad (3)$$

217 where $[E]_p$ is the concentration of an element in rainwater, $[E]_I$ is the con-
 218 centration of an element in irrigation water (mol kg^{-1} of water), and ρ_w is
 219 the specific mass of water ($\simeq 1 \text{ kg L}^{-1}$). Rainwater is here considered as

220 contributing negligibly to the supply of elements to the system, except for a
221 slight contribution for N, taken as constant from STICS.

222 The flux of inorganic element exported by drainage (Q_d) is given by:

$$Q_d = \rho_w D [E]_d, \quad (4)$$

223 where $[E]_d$ is the concentration of an element in soil solution (mol kg^{-1} of
224 water), D the drainage ($\text{mm} = \text{L m}^{-2}$ of water), and Q_d is in mol m^{-2} .

225 These equations are then used in PHREEQC simulation to calculate
226 fluxes of elements between soil, plant and soil solution. Eventually they allow
227 for computing the modifications of soil solution during its transfer through
228 soil from its entry via the irrigation channel till groundwater.

229 2.4. Proton balance

230 Acid / base reactions influence pH by a variety of reactions: exchange of
231 CO_2 between solution, soil atmosphere and external atmosphere, calcite dis-
232 solution / precipitation, N cycle and through nutrients absorption by plants
233 and excretion of protons in the rhizosphere. The rules for proton balance
234 have been established long ago, more specifically following acid rain studies
235 (Breemen et al., 1983; Bourrié and Lelong, 1990). The conservative function
236 is alkalinity, which is a linear combination of concentrations of cations conju-
237 gate from strong bases and anions conjugate from strong acids (Stumm and
238 Morgan, 1970; Bourrié, 1976). This linearity is conserved when converting

239 concentrations into fluxes via eq. 3 to 4. The flux of protons excreted by
 240 roots, *i.e.* the negative alkalinity flux into the solution, is implicitly modelled
 241 from the difference of bases uptaken and neutral salts uptaken as explained
 242 below, which takes thus into account the rhizosphere effect.

243 The influence of N cycle on the proton balance can be computed from the
 244 algebraic difference of fluxes : $([\text{NH}_4^+]_{\text{in}} - [\text{NH}_4^+]_{\text{out}}) - ([\text{NO}_3^-]_{\text{in}} - [\text{NO}_3^-]_{\text{out}})$
 245 (Breemen et al., 1983).

246 Ammonification can be written as:

247 and nitrification as:

248 so that the sum of reactions is:

249 For ammonium to be formed, according to reaction 5, a proton is con-
 250 sumed in the hydrolysis of amino-acid. If nitrogen is absorbed under ammo-
 251 niacal form, a proton is released at the root / solution interface, so that the
 252 proton balance is zero.

253 The oxidation of amino-acid into nitrate N(V) according to reaction 7

releases a proton. However, absorption of nitrate at the root / solution interface releases an OH^- in exchange, and therefore the proton balance is also zero. The balance is not zero for the topsoil if there are net fluxes either of NH_4^+ or of NO_3^- output to groundwater, which is expressed in the algebraic difference as proposed by Breemen et al. (1983).

The amount of absorbed charge by plants is positive as dominated by K^+ uptake. The plant compensates for this excess positive charge by the root proton transmission to the soil :

$$\Sigma[\text{H}^+] = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{NH}_4^+] - [\text{H}_2\text{PO}_4^-] - [\text{NO}_3^-] - 2[\text{SO}_4^{2-}], \quad (8)$$

so that the soil - plant system remains globally electrically neutral.

2.5. PHREEQC simulation

2.5.1. Processes simulated by PHREEQC in this paper

PHREEQC is used:

1. to compute saturation indexes SI of solutions with respect to minerals that can dissolve or precipitate;
2. to simulate the modifications of the chemical composition of soil solution when it equilibrates with minerals, *e.g.* calcite and apatite and including CO_2 , as $\text{CO}_{2(\text{g})}$ is formally treated as a mineral;
3. to simulate irreversible dissolution of P-K fertilizers;

- 272 4. to simulate nitrification as an input of nitric acid into solution, accord-
273 ing to reaction 7, which is equivalent to nitric acid dissolution;
- 274 5. to simulate the removal of some constituents from the solution: water
275 in order to simulate evaporation, specific minerals in order to simulate
276 uptake of inorganic elements (P, K, Ca, Mg, Na, S) by plants, and
277 nitric acid to simulate nitrate absorption by plants;
- 278 6. to compute by inverse modelling the best combination of geochemical
279 processes that explain the transformations of the soil solution in the
280 subsoil below the root system to groundwater.

281 *2.5.2. Dissolution of fertilizers and uptake by plants*

282 Dissolution of fertilizers and uptake by plants are respectively simulated
283 as an addition or a removal of the corresponding electrically neutral com-
284 ponent to soil solution, in the same way as evaporation is simulated with
285 a negative coefficient for water. To avoid transient negative concentrations,
286 fertilizer dissolution was simulated before absorption by plants.

287 Irreversible dissolution of fertilizers is simulated as dissolution of any min-
288 eral. The chemical composition of fertilizers is known and the mineral com-
289 ponents are derived from the chemical and mineralogical analyses of fertil-
290 izers and from the nature of industrial processes: (i) inorganic P fertilizers
291 consist of calcium di-hydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$, more soluble
292 than apatite and obtained by acid attack of apatite by sulfuric acid, with
293 gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, anhydrite CaSO_4 and bassanite $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ as

294 by-products; (ii) K fertilizers mainly consist of arcanite K_2SO_4 , and sylvite
295 KCl; (iii) N input from N cycle is simulated as an input of nitric acid HNO_3 .

296 The uptake of inorganic elements by plants is simulated here by PHREEQC
297 as follows: (i) P absorption by plants is simulated as the removal of calcium
298 di-hydrogen phosphate from the solution; (ii) S absorption by plants as the
299 removal of gypsum; (iii) calcium being absorbed in excess of the sum of P
300 and S, the remaining Ca absorption is simulated as CaO removal from the
301 solution ; (iv) Na, K and Mg absorption by plants are simulated as the re-
302 moval of Na_2O , K_2O and MgO from the solution; (v) N uptake is simulated
303 as nitric acid removal from the solution.

304 Calcium di-hydrogen phosphate, arcanite, sylvite, Na_2O , K_2O , CaO (lime),
305 MgO (periclase) and nitric acid were introduced in PHREEQC database as
306 PHASES; gypsum is already present in the database.

307 Activity coefficients were computed with Debye-Hückel extended law, as
308 ionic strength is small enough ($\simeq 0.01$ M). An example of calculation is
309 given as supplementary material in annex.

310 2.6. PHREEQC - STICS combination

311 The modifications of the chemical composition of soil solution from the
312 input in soil to its output to groundwater are simulated step by step. At
313 each step, the integration time is long enough for the change in storage in
314 soil (ΔS) to be negligible compared to the fluxes that pass through it; as a
315 result soil solution is considered as a node (Bourrié and Lelong, 1990). In

the case study (see below), the time step for crop growth is 1.5 to 2 months, which is the interval between two successive cuts.

Accordingly, the sum of fluxes entering solution (positive) is equal to the sum of fluxes leaving the solution (negative):

$$Q_p + Q_w + Q_b + Q_d = 0, \quad (9)$$

where Q_b is the flux exported to plants (biomass), Q_d the flux exported by drainage to the next node, Q_p the input flux by irrigation water from the previous node and Q_w the flux provided by fertilizers and / or mineral dissolution or precipitation. The boundary conditions fix the values of Q_p , inputs by irrigation and rain at the surface of soil and Q_d , drainage to groundwater below the root system, given by STICS.

The number of moles (n) of dissolved fertilizers per m^2 of irrigated meadow and relative to 1 kg of water that drains is derived by the following equations:

$$Q_w = \nu_E n, \quad (10)$$

where Q_w is the input flux by fertilizers, ν_E is the stoichiometric coefficient of element E in the fertilizer and n is the number of moles of fertilizer dissolved per m^2 . This assumes that fertilizers dissolve stoichiometrically.

The mass balance for any element E can be written as:

$$I\rho_w[E]_I + \nu_E n - R[E]_b - D\rho_w[E]_d = 0. \quad (11)$$

332 We chose potassium to calibrate the model, supposing that there is no
 333 net fixation of K^+ in soil (ion exchange) during the interval of cuts (several
 334 months), or that it is negligible, if any; the composition of fertilizers is then
 335 conventionally related to K^+ , so that $\nu_E = 1$ for K^+ . For K^+ , eq. 11 becomes:

$$I\rho_w[K^+]_I + n - R[K^+]_b - D\rho_w[K^+]_d = 0, \quad (12)$$

336 from which n is derived as:

$$n = D\rho_w[K^+]_d - I\rho_w[K^+]_I + R[K^+]_b. \quad (13)$$

337 Data and parameters necessary for the simulation of changes undergone by
 338 irrigation water in the meadows are given in Table 2 .

339 The results are presented as graphs in which soil solution is considered
 340 as a node (Bourri and Lelong, 1990) connecting different pools of elements
 341 (soil minerals, plants, fertilizers).

3. Material and methods

3.1. Case study

The Crau area is the study case, that was monitored during four years (2012-2015). Situated in Provence (South-East of France), its climate is mediterranean with a rainfall average about 550 mm/yr. Since the 16th century, water has been withdrawn from Durance River to this area, which has gradually constituted a dense network of channels (about 80 km long), hence enlarging irrigated area (Bonfillon, 2003). The Crau area is divided into i) the “dry Crau”, which is occupied by a natural steppe (9,200 ha) and ii) the “wet Crau” that is an irrigated area, mostly occupied by permanent grasslands (15,000 ha). Irrigation contributes to about 70-80% of the total recharge of the aquifer (Bourri et al., 2013; Oliso et al., 2013; Trolard et al., 2013a). Durance River deposited pebbles, which were cemented by calcium carbonate to form a pedogenetic puddingstone. Soils developed on this puddingstone are calcic luvisols (Bouteyre and Duclos, 1994), with a topsoil of 40 cm to 50 cm thick, containing a large content of pebbles (Colomb and Roux, 1978). The topsoil was progressively enriched in fine fractions due to silt input from the Durance River through irrigation period from April to September yearly till the 16th century.

Fertilization consists only of supplying P_2O_5 and K_2O for first and second cuts (Diehl and Denoy, 1942; Mohammed et al., 2016a). N input is mainly due to symbiotic fixation by Legumes with some delayed inputs by manure. Yield income is by three hay cuts per year, in May, June-July and August-

September respectively. In addition, a “fourth cut” is grazed directly by sheep in autumn and during the winter, but with a low value of digestibility. Thus the passage of sheep fertilizes grasslands with dung and urine, which represent a bulk mass of about 15 tons/ha to 30 tons/ha (Hugues et al., 1952). This area produces a high-value hay with a Certified Origin Product label (in french AOP), which is exported all around the world.

However, irrigated grassland areas in this study area are expected to decrease by 6 % to 11 % in 2030, because of land uses change, specially urban sprawl, which jeopardizes the sustainability of groundwater and permanent grasslands, and reduction of irrigation by about 30% due to allocation changes of water to other activities such as urban and industrial areas (Trolard et al., 2013a, 2016).

3.2. Crop model STICS operation

Simulations with STICS were made using its regional version where every irrigated grass fields ($\simeq 7000$ plots in the Crau area) were simulated within a multisimulation framework. Climate data were given by a station located at the domaine du Merle managed by the INRA-Agroclim unit. Soils characteristics were derived from the Arles soil map (Bouteyre and Duclos, 1994), and the irrigation history: irrigation dates back to the 16th century, and extended steps by steps (Bonfillon, 2003). Due to the silt input by irrigation water, thickness of A_p horizons increases with the age of irrigation (Trolard et al., 2016). Grass irrigation is made by flooding. Irrigation schedule is gov-

387 erved by water turns between April to September, which are usually fixed
388 every 10 days with an average intake of 200 mm. To characterize the irri-
389 gation agenda and harvesting agenda for all fields, a stochastic model was
390 implemented based on observations made in farms. Among the outputs, the
391 harvested biomass R and the drained water D were used in the study. The
392 yield estimates computed with STICS model were calibrated and validated
393 on a set of 80 plots where data were collected and measured during four
394 years (2006–2009) (Trolard et al., 2013b). The maximum uncertainties on
395 parameters calculated by STICS model were 5% for irrigation quantity, 3%
396 for biomass production and 10% for evapotranspiration.

397 3.3. Data collection and analytical methods

398 Meteorological data from INRA (Agroclim, Avignon) and Meteo France
399 stations were used in STICS model (minimum and maximum temperatures,
400 precipitation, solar radiation, wind speed and evapotranspiration of refer-
401 ence) to compute the yield (R) and drainage (D), for 2012-2015.

402 The data used in PHREEQC is the result of sampling field campaigns
403 during four years (2012-2015): irrigation water, groundwater, chemical com-
404 position of hay, mineralogy and chemical composition of fertilizers, collection
405 of historical chronicles (chemical analysis of hay, groundwater quality, climate
406 data).

407 For waters, temperature, pH and electrical conductivity EC were mea-
408 sured *in situ*; samples were filtered at 0.45 μm in the field; analyses of K^+ ,

409 Ca^{2+} , Na^{+} , Mg^{2+} were performed by atomic absorption spectrophotometry,
410 F^{-} , Cl^{-} , NO_3^{-} , SO_4^{2-} and PO_4^{3-} by ion chromatography, SiO_2 by the molybdate-
411 blue method and alkalinity was measured by acidimetric titration following
412 Gran's method (Gran, 1952). The maximum uncertainty for alkalinity was
413 0.01 mmol/kgH₂O and 0.1 pH unit for pH. The analytical precision for the
414 concentrations of major anions and cations ranges between 0.3 and 6.5 %.

415 For plants, analyses of major inorganic elements of the main families of
416 plants were performed by ICP dry residues on the three cuts of 2015 (at
417 INRA-USRAVE, Bordeaux laboratory, France). A database of the mineral
418 composition of the hay since 1960 has been built from analysis reports con-
419 ducted for the professional organization of Crau's hay Committee in accor-
420 dance to the specifications of originally protected designation of COP (in
421 french AOP) (Mohammed et al., 2016a).

422 For fertilizers, representative samples used in Crau were collected in 2014
423 and X-ray diffractometry was performed at ISTerre laboratory from Greno-
424 ble University. Chemical analyses of previous years were collected from the
425 Crau's hay Committee (Comité du foin de Crau, 2014). Enquiries were made
426 for fertilizer management, which supplied information about the inputs of
427 fertilizers (see Supplemantary material).

428 3.4. Goodness of fit

429 To test the goodness of the model, different types of assessment methods
430 were used to compare measured and simulated data. First, the correlation

coefficient R^2 was computed; it describes the data dispersion compared to the prediction. Then the root mean square error ($RMSE$), that gives an overall assessment of the difference and the mean bias error (MBE), that characterizes the bias of the difference, were used. Paired t-test was used by direct comparison between measured and simulated data using the null (H_0 measured and simulated data are not significantly different) and alternative (H_1) hypothesis. The Nash-Sutcliffe efficiency (EF) was computed to determine the relative magnitude of the residual variance ("noise") compared to the measured data variance ("information") (Nash and Sutcliffe, 1970). It can range from $-\infty$ to 1 and an efficiency of 1 ($EF = 1$) corresponds to a perfect match between simulated and observed data.

Index of agreement (d) is used to overcome the insensitivity of EF and R^2 to differences in the observed and predicted averages and variances (Legates and McCabe, 1999); d is the ratio of the mean square error and the potential error, its range is similar to that of R^2 and lies between 0 (no correlation) and 1 (perfect fit).

4. Results and Discussion

The chemical composition of irrigation water (Tables A1 to A5 in Supplementary material) shows only slight variations of Na^+ , Cl^- and SO_4^{2-} ; pH, Ca^{2+} , alkalinity and Mg^{2+} are quasi-constant. Phosphate, fluoride and ammonium concentrations were smaller than the detection limits. Nitrate concentrations are small, but non negligible, which implies there is some N-

leakage out of the system. Silica concentrations are small in between 2 and 5 mg SiO₂ kg⁻¹.

The chemical composition of groundwater shows even smaller variations; pH is lower, while inorganic C and N concentrations are larger than in irrigation water (Table A6 in Supplementary material). The chemical composition of hay shows systematic variations: the contents of inorganic elements increase from Cut1 < Cut2 < Cut3 (Table A7 in Supplementary material) (Mohammed et al., 2016a).

4.1. Mineral elements balances

STICS outputs, yield R , drainage D and factor of concentration of solution by evaporation f_c are given in Table A8 (Supplementary material), time step considered is the interval between cuts, with three cuts per year. Using equations 2 and 3, fluxes brought by irrigation water Q_I and exported by plants Q_b were computed.

Mass balance calculations show that irrigation water meets the plant mineral needs except for P and K (Table 3).

4.2. Check of equilibria with CO₂, calcite and gypsum

Saturation Indices of solutions with respect to CO₂(g), calcite and gypsum were computed with PHREEQC. Positions of irrigation waters and groundwaters in equilibrium diagrams (Fig. 3) show that :

- irrigation waters are oversaturated with respect to calcite;

- 474 • log of equilibrating partial pressure of CO₂ for irrigation waters is
 475 -3.25 ± 0.07 ($n = 12$), *i.e.* $\simeq 0.056\%$, which is slightly larger than
 476 atmospheric pCO₂, $\simeq 0.035\%$;
- 477 • groundwaters are close to equilibrium with respect to calcite ($SI =$
 478 0.1 ± 0.05);
- 479 • log of equilibrating partial pressure of CO₂ for groundwaters is -1.73 ± 0.19
 480 ($n = 36$);
- 481 • all solutions are under-saturated with respect to gypsum.

482 The implications are : (i) pH is buffered by solid / soil solution carbonate
 483 equilibria, which limits the natural tendency of soils towards acidification;
 484 (ii) large concentrations of calcium are present in solution and in soil; (iii)
 485 water quality is good, and salinity hazard is very small.

486 *4.3. Simulations of the modifications of the composition of solution during* 487 *its transfer through soil*

488 *4.3.1. Different steps of simulation*

489 Model is constrained by boundary conditions :

- 490 • input, irrigation water is slightly oversaturated with respect to calcite
 491 ($IS = 0.76 \pm 0.06$) as demonstrated above; this is due to the origin of
 492 Durance River from carbonated sediments (limestones, marls) in the
 493 Alps;

494 • output to groundwater of P is null (ADES, 2016), whereas P inputs by
 495 fertilizers are necessary to complete P brought by irrigation. Indeed,
 496 farmers bring P-K fertilizers with a slight excess of P with respect to K;
 497 as P concentration in groundwater is null, this implies that P in excess
 498 precipitates in the subsoil. As the geochemical environment is close
 499 to equilibrium with calcite, the most likely form of P precipitation is
 500 hydroxyapatite. This prevents phosphate to be transferred to ground-
 501 water, which would result in eutrophication as there is some nitrate
 502 leakage.

503 The simulations of soil solution are divided into four main steps repre-
 504 sented by four nodes (S) in the graph. Firstly, at S1 node (Fig. 4) irriga-
 505 tion water concentrates by evaporation and equilibrates with soil atmosphere
 506 $p\text{CO}_2 = 2 \times 10^{-2}$ bar. This last value is derived from groundwater *SI* com-
 507 puted by PHREEQC: as observed above, $\log p\text{CO}_2$ in phreatic groundwater
 508 shows very limited variations around -1.7 . We consider that irrigation water
 509 saturates soil pore space and infiltrates quickly. This limitates CO_2 diffusion
 510 to external atmosphere, and water stays in equilibrium with CO_2 - soil at-
 511 mosphere from the topsoil till the aquifer.

512 Then, at S2 and S3 nodes, soil solution equilibria are computed after
 513 dissolution of mineral fertilizers (N, P, K, Ca, S) and uptake of inorganic
 514 elements by plants, respectively. Finally at node S4, the soil solution drains
 515 below the root zone and relaxes to equilibrium with calcite and hydroxyap-
 516 atite. The work flow used for simulation in four steps is given in Fig. A5 in

517 Supplementary material.

518 4.3.2. Reference simulation: first cut 2015

519 For example for the first cut in 2015, over these steps, graphs of Ca,
520 pH, inorganic C and N balances are detailed in fig. 4. The initial chemical
521 composition of irrigation water is $1.683 \text{ mmol kg}^{-1}$ of Ca, $3.176 \text{ mmol kg}^{-1}$ of
522 inorganic C and $0.025 \text{ mmol kg}^{-1}$ of N, with $\text{pH} = 8.45$.

523 At S1 node, the irrigation water is diluted by rain water and then con-
524 centrated by evaporation. These two opposed effects directly determine the
525 concentration factor (f_c) according to eq. 1 so that $f_c = 1.34$.

526 This leads to an increase of concentrations of Ca, inorganic C and N in wa-
527 ter by $f_c = 1.34$ respectively to $2.255 \text{ mmol kg}^{-1}$ for Ca, to $4.256 \text{ mmol kg}^{-1}$
528 for inorganic C and to $0.034 \text{ mmol kg}^{-1}$ for N. This leads to an increase of
529 alkalinity with the same multiplying factor. As pH is an increasing func-
530 tion of alkalinity, pH is thus expected to increase, and consequently calcite
531 is expected to precipitate.

532 However, simultaneously, during infiltration in the topsoil (Horizon A),
533 irrigation water equilibrates with pCO_2 of the soil atmosphere, which is much
534 larger than pCO_2 in external atmosphere due to organic matter oxidation in
535 the soil. Therefore, changes in the chemical composition of water are the
536 result of two opposite processes:

- 537 • concentration by evaporation of a saturated water tends to favor the
538 increase of pH (Harvie and Weare, 1980), since the alkalinity is positive,

539 and to precipitate calcite;

540 • dissolution of CO_2 tends to lower the pH and dissolve calcite.

541 The simulation shows that this latter phenomenon dominates: a small amount
542 of CO_2 dissolves and provides 0.137 mmol of C and leads to calcite disso-
543 lution that provides 0.432 mmol of Ca. These modifications keep the soil
544 solution in equilibrium with calcite, although irrigation water was initially
545 over-saturated, and can be explained by the fact that the residual alkalinity
546 of calcite in irrigation water is negative (Al-Droubi et al., 1980). As a result
547 pH decreases to 7.13.

548 Then this solution is brought back to 1 kg of water by identically mix-
549 ing the resulting solution with itself, in order to keep the mass reference
550 to 1 kg of water. Thereafter, the volume of water does not change and the
551 concentrations can be directly compared with groundwater composition.

552 Statistical Student test ($P = 0.05, \nu = 36$, Table A9 in Supplementary
553 material) shows that composition of soil solution at node 1 is not significantly
554 different from groundwater for Na^+ , Cl^- , SO_4^{2-} , K^+ and pH; it is significantly
555 different for inorganic C, Mg^{2+} and Ca^{2+} and even more for NO_3^- , as nitrate
556 concentration is ten times larger in groundwater as compared to irrigation
557 water.

558 This means that: (i) *even before taking into account fertilizers dissolution*
559 *and uptake by plants*, for most major elements, by equilibrating with soil at-
560 mosphere pCO_2 and concentrating by evaporation, soil solution becomes very

close to groundwater and (ii) that some significant, though minor, changes occur during its transfer through soil and puddingstone. These changes are then simulated to improve the fits.

Hereafter simulation of water quality divides into two steps, first inputs of inorganic elements are added to the solution from fertilizers and manure (node S2), secondly elements are removed from the solution by plants (node S3). At S2 node, dissolution of fertilizers adds 0.147 mmol Ca. The amount of dissolved fertilizer was fitted on the concentration of K^+ in groundwater, and it was simply assumed that fertilizers dissolve proportionally to the average composition of the P-K fertilizer. This results in a slight excess of P addition, as the ratio P/K in fertilizers added is larger than the ratio P/K in the plant requirement.

At S3 node, roots absorb 0.236 mmol Ca and other nutrients, excreting H^+ , which acidifies the solution: pH decreases to 6.7. Fertilizer application quasi-exactly compensates nutrient requirements.

Finally at S4 node, the drainage water before reaching the groundwater equilibrates with respect to calcite, hydroxy-apatite and pCO_2 , as this was the boundary conditions fixed : (i) calcite dissolution occurs, which adds 0.444 mmol Ca and C, and (ii) slight amount of P reaches the groundwater, which is simulated as precipitation as hydroxy-apatite (Table 4); the simulation of apatite precipitation is quantified as an irreversible fixation of 0.016 mmol Ca; (iii) degassing releases 0.636 mmol CO_2 , which leads to increase pH to 7.11.

584 4.3.3. *Results for second and third cuts*

585 The results obtained for the second cut (Cut2) are similar to the results
586 for the first cut (Cut1), but this is not the case for the third cut (Cut3)
587 (see graphs Fig. A1 to A4 in Supplementary material). The major difference
588 is that there is no addition of industrial fertilizers, whereas dissolved (P-K)
589 from grazing manure added in winter, becomes progressively available (Kang
590 and Freeman, 1999).

591 4.3.4. *Graphs of mass balances and pH*

592 Graphs of mass balances of Ca and inorganic C and of pH changes were
593 drawn for the three cuts and four years (Fig. in supplementary materials).
594 They show the sequence of geochemical processes that modify the chemical
595 composition of water from irrigation water to groundwater. It appears that
596 the irrigated agricultural system has the side effect of buffering pH of soil
597 solution by bringing carbonate; moreover, both in the topsoil and in the
598 subsoil, calcite dissolves: pH is buffered by equilibrium with calcite in a
599 pH range from 7 to 8.3, depending on the partial pressure of CO₂ in soil.
600 Carbonate input by irrigation water amounts to 75% of the carbonate content
601 of groundwater. This has a positive effect in maintaining soil quality and
602 fertility, as it opposes to the general geochemical tendency to decarbonation
603 in the north of Mediterranean sea, to acidification and degradation of clay
604 minerals and soil structure.

605 Irrigation can affect soil carbon storage by altering both soil organic car-

606 bon (SOC) and soil inorganic carbon (SIC) cycling (Hannam et al., 2016).

607 Here, we only discuss soil inorganic carbon.

608 During the water quality transformation, which takes place in the upper
609 horizon of soil (Horizon A), irrigation water dissolves calcite and $\text{CO}_{2,g}$ of
610 the soil atmosphere to maintain the soil solution at equilibrium with calcite,
611 although irrigation water was initially supersaturated with respect to calcite.
612 For 2015 Cut 1, to obtain 1 L of groundwater, irrigation water starts with
613 1.34 L, and therefore 1.37 mmol of CO_2 (g) of the soil atmosphere is trapped.
614 Then, the solution re-equilibrates with the calcite, since there is a stock
615 of “active limestone” in soil and in the calcrete (locally termed “taparas”).
616 As a result, 0.444 mmol of calcite dissolve and 0.635 mmol of $\text{CO}_{2,g}$ degas,
617 which returns to the soil atmosphere per 1 kg of drained water below the root
618 system.

619 The balance is that 0.735 mmol of $\text{CO}_{2,g}$ per 1 kg of drainage water is
620 dissolved and transformed into HCO_3^- anion and drained to the groundwater.
621 The soil solution therefore plays here *locally* the role of CO_2 sink. However,
622 this results from calcite dissolution:

623 and calcite is expected to precipitate later, either in the subsoil or in the
624 sedimentary basin. Then the reverse reaction will occur, so that ultimately
625 the small amount of CO_2 trapped in soil will be released to atmosphere. The

net balance is thus zero, and this does not act *globally* as a carbon sink. Only calcium originating from Ca-silicates weathering can trap CO₂ from the atmosphere.

4.4. Simulated and measured data

4.4.1. Global fit

The excellent correlation ($R^2 \geq 0.956$) obtained between measured and simulated values of groundwater validates the proposed approach. This is illustrated in Fig. 5 and Table in Annex, with the results of statistical tests of goodness of fits. A further scrutiny of Fig. 5 shows that all elements are close to the 1:1 line. K cannot be used for validation, as it was used to fit the number of moles of fertilizers dissolved and our model was fitted on the concentration of K⁺ in groundwater. Na⁺, Cl⁻, SO₄²⁻ and inorganic C do not show any appreciable deviation. Instead, Ca and Mg show a slight but net deviation. The differences (Table 5) are nearly exactly opposite, with [Ca²⁺] being slightly underestimated ($\Delta = 0.237 \text{ mmol kg}^{-1}$) and [Mg²⁺] being slightly overestimated, ($\Delta = 0.234 \text{ mmol kg}^{-1}$). The discrepancy for Ca could neither be solved by modifying pCO₂ in the simulation, nor by allowing calcite to precipitate with some oversaturation degree. This would lead to a poorer fit for inorganic C. It is thus likely that some Mg is fixed in soil and some Ca released in the solution by ion exchange on clay minerals or exchange sites of organic matter, which was not included in the direct simulation above.

648 4.4.2. Inverse modelling

649 Inverse modelling was used to simulate the modification from node S3,
650 just after plant uptake, to groundwater, by introducing ion exchange, and
651 letting all minerals, *i.e.* calcite, hydroxy-apatite and $\text{CO}_{2(\text{g})}$ free to dissolve or
652 precipitate, $\text{CO}_{2(\text{g})}$ being formally treated as a mineral. PHREEQC can com-
653 pute the amounts of dissolved or precipitated minerals that account better to
654 explain the transformation of soil solution at S3 node into groundwater. The
655 results show that ion exchange contributes to Ca release ($3 \times 10^{-4} \text{ mol kg}^{-1}$
656 of water), against Mg ($-2 \times 10^{-4} \text{ mol kg}^{-1}$ of water), Na ($-2 \times 10^{-4} \text{ mol kg}^{-1}$
657 of water) and quite negligible K ($-5 \times 10^{-6} \text{ mol kg}^{-1}$ of water) fixation; some
658 $\text{CO}_{2(\text{g})}$ escapes and excess P precipitates as apatite. All fits are better than
659 10% agreement between groundwater simulated and observed (Table 5).

660 4.5. Sustainability

661 Due to its chemical composition, irrigation water supplies most of nutri-
662 ents necessary to hay growth. It is completed by some P, K fertilizers and N
663 input from manure and recycling of N from soil organic matter. A slight ex-
664 cess of P precipitates as hydroxy-apatite in the soil or subsoil. Ion exchange
665 fix some Mg and Na against some Ca release, with a quasi-negligible K fix-
666 ation, which justifies our hypothesis to fit the amount of fertilizers dissolved
667 on K output.

668 Globally, some calcite dissolves, which is the general tendency. It is slower
669 than it would be under rainwater input alone, as irrigation water originates

670 from the Alps, where limestones are abundant.

671 The nutrient status of soils is thus preserved, with some enrichment in P
672 and stability of K status, in a context of possible decrease of the availability
673 of P and K resources at a global level.

674 Groundwater quality is preserved, with a small leakage of nitrate, but *ca.*
675 9 mg N Liter⁻¹, which is much smaller than the limit for drinking water. P
676 is retained in soil, which prevents from eutrophication.

677 The present agro-ecosystem preserves thus both soil and water resources,
678 in a region submitted to large pressures from urban sprawl, in the immediate
679 vicinity of Marseilles, Arles and several cities. It dates back to the 16th
680 century and is the basis for many labelled productions (hay, lamb, wool...).
681 It appears thus as a sustainable and productive agro-ecosystem.

682 5. Conclusions

683 The combination of a crop model STICS and a geochemical model PHREEQC
684 allows for modelling and quantifying the changes in chemical composition of
685 water from the surface till the aquifer by including together data from agron-
686 omy, climatology, geochemistry and soil science. The approach consists to:
687 (i) compute step by step the successive modifications of the chemical com-
688 position of water, considered as a node from its input in the agrosystem till
689 the groundwater in the aquifer; (ii) introduce the plant uptake in the geo-
690 chemical model PHREEQC; (iii) compute the flux and the mass balance for
691 all chemical elements and parameters defining the water and soil quality of

692 agrosystem, and (iv) use PHREEQC as inverse model to quantify geochem-
693 ical processes below the root zone.

694

695 The proposed model was tested and validated on four years of cultivation
696 of hay and for each cut per year in Crau area.

697 Results show that the main determinants of the chemical changes of water
698 composition during its transfer through soil are: concentration by evapora-
699 tion, equilibration with $p\text{CO}_2$ of soil atmosphere, mineral uptake by plants,
700 input of fertilizers, grazing by sheep during the winter and mineral-solution
701 interactions in superficial formations, including ion exchanges, till the aquifer.
702 Except for N, the mineral requirements of hay are largely covered by dis-
703 solved elements brought by irrigation water with only slight deficits in K
704 and P, which are compensated by P-K fertilizers and the pasture by sheep
705 during winter. For groundwater, measured composition fit statistically very
706 well with those computed, validating thus this approach.

707 This long-term established agrosystem protects both soil and water resources:
708 soil nutritional status remains constant with even some enrichment in P as
709 apatite precipitation in soil or subsoil, a net Mg fixation and a slight K
710 fixation (at least a stability) on exchange sites; long-term decarbonatation
711 occurs as is the rule north of Mediterranean sea and in temperate climate, but
712 it is largely slowed by the input of dissolved carbonate in irrigation water,
713 originating from Alps's limestones; groundwater quality is preserved from
714 eutrophication by P fixation in soil due to the large concentration of Ca in

715 solution and in soil.

716 Aqueous geochemistry of this agrosystem reveals that irrigation via Durance
717 River provides beneficial effects such as savings of fertilizers, protection of
718 soil minerals against natural tendency to acidification, groundwater recharge
719 and control of groundwater quality. In addition it contributes to production
720 of a high quality forage (COP, in french AOP). This long-terme crop system
721 established back to the 16th century can thus be considered as a remarkable
722 instance of ecologically intensive agriculture.

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1050 List of Tables

1051	1	Characteristics of models connecting agronomy, climatology,	
1052		geochemistry and soil science.	56
1053	2	Biogeochemical processes modelled and necessary data for the	
1054		“Irrigation water – atmosphere – plant – soil – groundwater”	
1055		system.	57
1056	3	Mass balance of inputs by irrigation water and uptakes by	
1057		Crau’s hay.	57
1058	4	Flux of P in $\mu\text{mol}/\text{m}^2$ through simulation steps of biogeochem-	
1059		ical modelling.	58
1060	5	Comparison of simulated soil solution for steps S1, S3 and S4	
1061		with groundwater, concentration in mmol/l	58

1062 List of Figures

1063	1	Factors acting in the system	54
1064	2	model	55
1065	3	Diagrams of Saturation Index of solutions with respect to cal-	
1066		cite and gypsum	59
1067	4	Ca and C mass balance and pH changes	60
1068	5	Comparaison of simulated and measured annual values of ground-	
1069		water	61

Figure 1: Factors affecting the chemical composition of water in the Crau's agrosystem.

Figure 2: Architecture of the combination of the crop model STICS and the geochemical model PHREEQC, necessary data for inputs and main outputs obtained after simulations.

Table 1: Characteristics of models connecting agronomy, climatology, geochemistry and soil science.

Modelling/Model	Aim	Agr.	Clim.	Geoch.	Soil Sci.	Ref.
Hydrological and bio-geochemical model	N cycling and transport	x	x	x	x	1
Hydrological and bio-geochemical model	Solute retention	x		x	x	2
Biogeochemical models: PaSim /Biome-BGC MuSo	C cycle	x	x	x	x	3
Terrestrial biosphere models (TBMs)	C cycle	x	x			4
Biogeochemical modelling	Nutrients cycling affected by wildfire	x		x		5
Hydrochemical model: AHM	Daily stream chemical composition and its reaction to N deposition	x	x	x	x	6
SOILVEG-GRO/NUCSAM	Effects of multiple stressors on forest stands	x	x	x		7
"Ecosystem (DayCent)/chemical model (PHREEQC)"	"Atmospheric deposition impacts "	x	x	x	x	8

Agr. = Agronomy / Ecology / Biology; Clim. = Climatology; Geoch. = Geochemistry; Soil Sci. = Soil Science and Hydrology.

1. (Cirimo and McDonnell, 1997); 2. (Valett et al., 1996; Dahm et al., 1998); 3. (Sándor et al., 2016); 4. (Xiao et al., 2012; Cramer et al., 1999; Jung et al., 2007; Huntzinger et al., 2012); 5. (Fultz et al., 2016); 6. (Meixner et al., 2000); 7. (van Heerden et al., 1995; Mohren and van de Veen, 1995); 8. (Hartman et al., 2007).

Table 2: Biogeochemical processes modelled and necessary data for the “Irrigation water – atmosphere – plant – soil – groundwater” system.

Processes	Equation and necessary data
Irrigation water	Water analysis
Concentration by evaporation	$f_c = \frac{I+P}{I+P-ET} = \frac{I+P}{D}$, I = Irrigation, P = Precipitation, ET = Evaporation D = Drainage, $D = I + P - E$.
pCO ₂ influence	pCO ₂ and soil temperature (t)
Fertilizers dissolution	Stoichiometry of Fertilizers P - K, fertilizers analysis
Rate of fertilizers dissolution	Calibration by K uptake $n = D\rho_w[K]_d - I\rho_w[K]_0 + R[K]_b$ R =Yield, D = Drainage, ρ_w = specific mass of water.
Mineral uptakes	Balance of absorbed elements and excreted protons : $\Sigma[H^+] = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] - [NO_3^-] - [H_2PO_4^-] - 2[SO_4^{-2}]$
Soil / solution interactions	Minerals nature and thermodynamic conditions (equilibrium / non equilibrium / kinetic, pCO ₂ , temperature).
Output to groundwater	$\rho_w[E]_d = \frac{I}{D}\rho_w[E]_I - \frac{R}{D}[E]_b + v_E \frac{n}{D}$

Table 3: Mass balance of inputs by irrigation water and uptakes by Crau’s hay.

	Cut	Ca	Mg /mmol/m ²	P	K	Na	S
Q_I	Cut1	2.862	0.648	0.001	0.046	0.799	1.077
	Cut2	2.707	0.757	0.004	0.042	0.757	1.093
	Cut3	2.615	0.741	0.002	0.040	0.668	0.893
Q_b	Cut1	-0.067	-0.025	-0.019	-0.125	-0.041	-0.016
	Cut2	-0.078	-0.031	-0.021	-0.107	-0.031	-0.018
	Cut3	-0.085	-0.033	-0.021	-0.082	-0.040	-0.016
Balance	Cut1	2.795	0.623	-0.018	-0.079	0.758	1.060
	Cut2	2.629	0.726	-0.017	-0.065	0.726	1.075
	Cut3	2.530	0.708	-0.019	-0.042	0.628	0.877

Q_I Fluxes brought by irrigation; Q_b Fluxes exported by hay.

Table 4: Flux of P in $\mu\text{mol}/\text{m}^2$ through simulation steps of biogeochemical modelling.

	Cut	Irrigation water	Fertilizers addition	Root uptake	Precipitated as hydroxy-apatite	Groundwater
2012	C1	0	54	-32	-22	0.4
	C2	0	81	-55	-25	0.3
	C3	0	56	-53	-2	0.4
2013	C1	0	64	-32	-31	0.4
	C2	0	67	-40	-26	0.3
	C3	0	56	-53	-2	0.4
2014	C1	0	73	-37	-36	0.5
	C2	0	120	-66	-53	0.3
	C3	0	96	-92	-4	0.4
2015	C1	0	98	-49	-48	0.4
	C2	0	110	-85	-30	0.3
	C3	0	88	-57	-30	0.3

Table 5: Comparison of simulated soil solution for steps S1, S3 and S4 with groundwater, concentration in mmol/l.

	Ca	Mg	Cl	K	Na	S	C	N
Aquifer av.	3.443	0.473	0.640	0.033	0.639	1.225	5.403	0.625
Aquifer sd.	0.19	0.05	0.01	0.01	0.05	0.13	0.80	0.12
S1	2.718	0.774	0.648	0.031	0.995	1.122	5.939	0.079
S3	2.629	0.707	0.660	0.038	0.824	1.337	5.939	0.625
S4	3.206	0.707	0.660	0.038	0.824	1.337	5.616	0.625
Inverse model	3.633	0.473	0.660	0.033	0.639	1.337	5.508	0.625

S1 = soil solution after evaporation, equilibration with calcite and $\text{CO}_{2(\text{g})}$; S3 = soil solution after fertilizers (N, P, K) dissolution and plant uptake; S4 = soil solution after equilibration with calcite, hydroxy-apatite and $\text{CO}_{2(\text{g})}$. Inverse model optimizes mass transfer to account for transformation of solution S3 to the aquifer.

Figure 3: Diagrams of Saturation Indices (SI) of solutions with respect to calcite (left) and gypsum (right) of irrigation water (red) and groundwater (blue). Points above the equilibrium line indicate oversaturation and points below undersaturation.

60

Figure 4: Mass balance and fluxes of Ca, inorganic C, and N and pH variations for 2015 Cut1 in mmol/kg for 1 kg of water draining till the aquifer through the soil horizons in the Crau's agrosystem.

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Figure 5: Comparaison of simulated and measured values of chemical composition of the Crau's groundwater (C, Ca, Cl, K, Mg, Na, S in mmol/L). Red line = 1:1 line; black line = regression line of data.